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(71) Applicant: **SILVERRAY LTD** [GB/GB]; Unit F8 (5th Floor), Pear Mill Industrial Estate, Stockport Road West, Stockport Greater Manchester SK6 2BP (GB).

(72) Inventor; and

(71) Applicant *(for US only)*: **SILVA, Sembukuttiarachilage Ravi Pradip** [GB/GB]; c/o Silverray Ltd, Unit F8 (5th Floor), Pear Mill Industrial Estate, Stockport Road West, Stockport Greater Manchester SK6 2BP (GB).

(74) Agent: **CHAMBERS, Neil**; Burrows Chambers Associates, Business Centre West, Avenue One, Business Park, Letchworth Garden City Hertfordshire SG6 2HB (GB).

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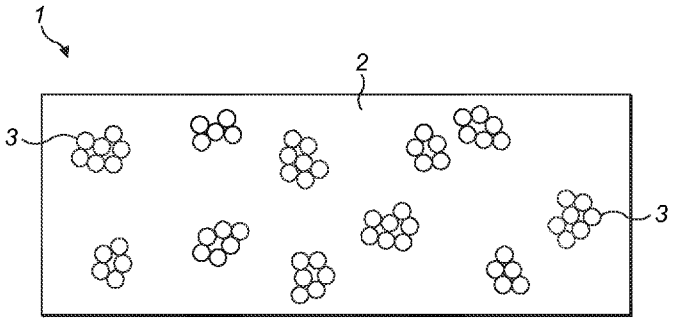

FIG. 1

(57) **Abstract:** A device (1) for converting incoming radiation into positive and negative electrical charges, the device comprising: a network (2) comprising: a first semiconductor material for transporting positive electrical charges; and a second semiconductor material for transporting negative electrical charges. The first and second semiconductor materials being dispersed within the network to provide a plurality of electrical junctions, wherein, the network further comprises a plurality of nano-structured agglomerates (3) dispersed within the network, the nano-structured agglomerates (3) comprise a plurality of regions and/or interfaces of different relative permittivity capable of creating dielectric inhomogeneities within the nano-structured agglomerates.

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Radiation Detector

The present invention relates to radiation detection, in particular radiation detection apparatus and associated method(s). The present invention further relates to a device, apparatus and method for converting incoming radiation into positive and negative electrical charges.

The widespread use of ionising (e.g. nuclear) radiation for a range of applications, such as in radiation therapy, security screening and industrial applications such as non-destructive testing (NDT), has necessitated the development of appropriate radiation detection techniques. Here both the terms "ionising radiation" and "nuclear radiation" are considered to extend to alpha particles, beta particles, X-rays, gamma rays and so on. Common nuclear radiation detectors comprise semiconductor devices, typically silicon (Si) or germanium (Ge). These solid-state devices detect nuclear or ionising radiation by measuring the number of charge carriers (electrons and holes) generated in the detector volume in response to incident radiation. When high-energy radiation photons or particles collide with the active semiconductor material in the detector, it causes ionisation and creates charge carriers. Ionisation is created by charge being generated within the device structure as a result of external radiation either displacing electrons from core-shells of the atom or high-speed radiation interacting with solid matter. The generated charge carriers are accelerated under the influence of an electric field generated by an applied voltage bias. This leads to an electric current which can be readily collected at electrodes. Current can be found to be proportional to the radiation dose deposited in the material. Depending upon the energy of the photons of incident radiation and the atomic number (Z) of the material, there are three main mechanisms through which matter is widely attributed to interact with the incoming photons, namely, the photoelectric effect, Compton scattering and pair production. Detectors typically measure the amount of radiation incident, the spatial distribution, the radiation spectrum and other properties.

Solid-state inorganic radiation detectors based on silicon are known. Despite the excellent performance of inorganic detectors, they suffer from major drawbacks owing to the crystalline detector materials used, such as the manufacturability of curved geometries, brittle active materials, high manufacturing costs and limited detector size. In comparison to their better established inorganic counterparts, organic semiconductors (e.g. semiconducting polymers) present several advantages which make them an attractive candidate for large area, low-cost electronics. Inks consisting of these organic semiconductors can be prepared by dissolving conjugated polymers, oligomers and small molecules in common organic solvents. These inks can then be simply coated onto substrates using conventional wet processing techniques, leading to the possibility of large area device production at extremely low cost. Owing to their flexible nature, large area organic semiconductor based detector panels can be formed to curved geometries, such as tubes, to place around piping to monitor radioactive fluids, for example. Flexible organic dosimeters can also be used for patient dosimeters, for X-ray diagnostics or cancer therapy, for example, by forming large area pixelated detector tubes around parts of a patient's body, such as a limb, to provide localised spatial-resolved dose measurements.

Some features of known high-energy radiation detectors include low dark current (leakage current), good rectification behaviour, high charge-carrier mobility and high radiation stopping power. Generally, radiation detectors can be sub-categorized as 'direct' or 'indirect' detectors.

Previously it has been shown that radiation-induced photocurrent can be achieved using single homogeneous materials such as poly-(triarylamine) (PTAA), poly([9,9-dioctylfluorenyl-2,7-diyl]-co-bithiophene) (F8T2), etc. in a metal/semiconducting polymer/metal device architecture in direct radiation detectors. Such materials are active polymer materials, but they are only capable of carrying a single type of charge (electron or hole). The mono-carrier nature of devices incorporating single homogeneous materials (single organic semiconductor systems) reduces the overall signal response that can be achieved. The organic semiconductors typically consist of low atomic number (low Z) carbon and hydrogen constituent atoms, which results in a low stopping power (attenuation) for high-energy radiation. Therefore, this means that, for an organic material detector to operate efficiently, it needs to be very thick so there are enough ionisation events created in order to produce a suitable current that can be detected. Yet, as the mobility of the detected carriers is so low within organic materials (typically polymeric materials insulate owing to a lack of free carriers and have a low charge mobility), at a higher thickness, the efficiency at which the charge can be swept across is low and very high fields are needed. These high fields may breakdown the material and, so, it is difficult to produce a compromise structure that has high ionisation, as well as high collection efficiency.

In the case of typical semiconductor devices such as silicon, one can have a high charge mobility and a small ionisation cross-section for radiation detection. Therefore, one can have much thicker silicon radiation detectors; however, this makes them highly rigid and brittle. Further, high electric fields are needed in order to sweep the ionised charge carriers, owing to radiation interactions across the device, and would make for expensive devices having electric fields that are incompatible with standard CMOS IC (complementary metal–oxide–semiconductor integrated circuits) circuits. Further, indirect bandgap also makes the radiation capture less efficient within these devices, which naturally would have small foot-prints owing to the additional processing needed in the silicon wafers.

Present polymer and organic solar cells exhibit relatively low efficiency. Although, over time, these technologies have been developed and efficiencies of between 10-20% power conversion efficiency may now be routinely obtained.

As such, these solar cell devices may be reasonably efficient, if made in thin film format with a thickness of the order of 100nm to 10micron and, owing to the organic or polymer materials used to produce most of the device, provide flexibility and the advantage of large area manufacture. However, owing to the lower efficiency of the organic/polymer to stop X-ray or gamma radiation, the devices cannot generally be used in radiation detection.

The Applicant has previously shown and demonstrated in a previous Patent Application how incorporating Bismuth Oxide nano-particles (NPs) – together with other nano-particles and nanostructures with much higher Z-number compared to the polymers of a bulk heterojunction (BHJ) – within the active heterojunction area of an organic or polymer solar cell attenuates an X-ray radiation signal and creates sufficient electron-hole pairs to be swept across the diode-like device in order to create an efficient X-ray detector.

It was demonstrated that device efficiency increases with an increase in nano-particle percentage, such that, with more attenuation of the radiation, a higher detector current results. However, increasing NP percentage has a negative effect and such an increase results in loss of flexibility of the organic / polymer detector, leading to it being more rigid, such that it would no longer be considered a flexible

material that can be processed using solution processable large-area techniques. Detectors therefore must strike a compromise between increasing the cross-sectional depth of the active capture portion of a detecting component, and device flexibility and processability.

The present invention seeks to address at least some of the problems outlined above.

According to a first aspect, the invention provides a device for converting incoming radiation into positive and negative electrical charges, the device comprising:

a network comprising:

a first semiconductor material for transporting positive electrical charges; and

a second semiconductor material for transporting negative electrical charges,

the first and second semiconductor materials being dispersed within the network to provide a plurality of electrical junctions,

wherein, the network further comprises a plurality of nano-structured agglomerates dispersed within the network, the nano-structured agglomerates comprise a plurality of regions and/or interfaces of different relative permittivity capable of creating dielectric inhomogeneities within the nano-structured agglomerates.

Preferably, the nano-structured agglomerates comprise a plurality of regions of different relative permittivity comprising interface regions comparable to, or within, a wavelength of said incoming radiation.

Preferably, the nano-structured agglomerates comprise a plurality of regions of different relative permittivity substantially distributed throughout and/or across the agglomerates.

Preferably, the nano-structured agglomerates comprise a plurality of interface regions substantially distributed throughout and/or across the agglomerates.

Preferably, the nano-structured agglomerates comprise two or more interfaces or interface regions within a distance of a wavelength of said incoming radiation, preferably at least in any one direction.

Preferably, the nano-structured agglomerates comprise a porosity or void fraction of about 0.01 to about 0.99, of about 0.05 to about 0.7, or about 0.1 to about 0.3.

Preferably, the nano-structured agglomerates comprise:

one or more, or a plurality of, solid nano-particle structures; and

one or more, or a plurality of, voids between the one or more, or plurality of solid nano-particles structures.

Preferably, the voids are air or vacuous.

Preferably, the agglomerates are capable of speeding up and slowing down received radiation, creating one or more, or a plurality of positively or negatively charged puddles within surface structures of the agglomerates.

Preferably, the surface structures of the agglomerates, whether external and/or internal surface structures, are capable of interacting with incoming radiation to attenuate the radiation and provide improved conversion to positive and negative electrical charges.

Preferably, the nano-structured agglomerates are configured to act as local inhomogeneities capable of attracting and concentrating the electric field.

Preferably, nano-structured agglomerates are configured to convert said radiation into positive and negative electrical charges in radiation-agglomerate interaction events.

Preferably, nano-structured agglomerates comprises a size in the range of 20-100 nm, being preferred for detection of X-ray radiation.

Preferably, the nano-structured agglomerates are doped nano-structured agglomerates, having additional electron-containing or hole-containing elements.

Preferably, nano-structured agglomerates are doped with Caesium (Cs) and/or Lanthanum (La).

Preferably, the doped nano-structured agglomerates are configured to increase and/or decrease the charge carriers within the nano-structured agglomerates.

Preferably, the doped nano-structured agglomerates comprises light to heavy dopant atoms.

Preferably, the plurality of nano-structured agglomerates comprises optimised parameters of one or more of the following group, comprising:

nano-particle and/or agglomerate size;
nano-particle and/or agglomerate distribution;
void fraction of the nano-structured agglomerates; and/or
doping.

Preferably, the first and second semiconductor materials are:

organic-organic transport materials;
inorganic-inorganic transport materials; or
organic-inorganic transport materials.

Preferably, the nano-particles comprise:

high-Z nano-particles;
organic nano-particles; or
combinations thereof.

Preferably, particles of the first and/or second semiconductor material(s) are sized and intended to agglomerate, the first and/or second semiconductor material(s) providing nano-particles for agglomeration without requiring (further) addition of nano-particles to form the matrix.

Preferably, the network is a bulk heterojunction.

Preferably, the incoming radiation comprises ionising radiation. Further preferably, the incoming radiation comprises one or more of alpha particles, beta particles, neutrons, X-rays and gamma rays. Accordingly, and preferably, the plurality of regions of different relative permittivity comprise regions and/or interfaces that are comparable to, or within, a wavelength of alpha particles, beta particles, neutrons, X-rays and/or gamma rays.

Preferably, parameters of the nano-structured agglomerates are configured to be actively optimised for detection of defined wavelengths or forms of radiation intended to be detected by the device.

Preferably, the first semiconductor material comprises P3HT, the second semiconductor material comprises PCBM, and the nano-particles comprise Bi_2O_3, optionally doped with Caesium (Cs) and/or Lanthanum (La).

Preferably, a plurality of regions of different relative permittivity may be created using the phenomena of plasmonics. Most preferably, plasmonics comprises creating surface charge waves in the network, particularly in small particles having metallic surfaces or regions.

According to a second aspect, the invention provides a radiation detector comprising:

a first electrode;

a second electrode; and

a device according to the first aspect located or sandwiched between the first and second electrodes.

Preferably, the radiation detector comprises a current measuring device.

Preferably, the radiation detector comprises a voltage source.

Further preferably, the radiation detector comprises a wireless transmitter that enables real-time data transmission to a remote computer.

Preferably, the radiation detector comprises a display for indicating radiation levels.

According to a third aspect, the present invention provides a system comprising a plurality of radiation detectors according to the second aspect.

Preferably, the system comprises a plurality of radiation detectors according to the second aspect, wherein at least some of the plurality of radiation detectors are configured to:

detect multiple different types of radiation;

detect one type of radiation; and/or

identify different energies of a particular radiation.

Preferably, the device or radiation detector is integrated either on a rigid backing or a flexible backing.

According to a fourth aspect, the invention provides a method comprising:
using a device according to the first aspect, a radiation detector according to the second aspect, or a system according to the third aspect to convert incoming radiation into positive and negative electrical charges; and
recording a characteristic generated by the positive and negative electrical charges.

Preferably, the method further comprising converting the incoming radiation into free positive and negative electrical charges in radiation-agglomerate interaction events.

Preferably, current is generated in response to the application of a voltage across the device. Further preferably, converting recorded current into an estimate of a level of radiation.

According to a fifth aspect, the present invention provides a process for providing a network for a device for converting incoming radiation into positive and negative electrical charges, the process comprising:

dissolving first and second semiconductors in one or more solvents, the first and second semiconductors being capable of transporting positive and negative electrical charges, respectively;

adding a plurality of nano-particles and dispersing the plurality of nano-particles to form a matrix; and

agglomerating the nano-particles in the matrix to form a plurality of nano-structured agglomerates, the nano-structured agglomerates comprising a plurality of regions and/or interfaces of different relative permittivity, being capable of creating dielectric inhomogeneities within the nano-structured agglomerates.

Preferably, the method comprising creating:

a plurality of regions and/or interfaces of different relative permittivity comparable to, or within, a wavelength of said incoming radiation;
one or more, or a plurality of, solid nano-particle structures; and
one or more, or a plurality of, voids between the one or more, or plurality of solid nano-particles structures.

Preferably, the nano-structured agglomerates are formed:
at least partially within the matrix, prior to application to a substrate; and/or
during layering of the matrix upon a/the substrate.

Preferably, the method comprising creating:
one or more, or a plurality of, solid nano-particle structures; and
one or more, or a plurality of, voids between the one or more, or plurality of, solid nano-particles structures.

Preferably, agglomeration comprises controlling:
solvents, anti-solvents, cations, anions, temperature and/or time at which different components are introduced;
a speed at which the solvents are mixed; and/or
an environment in which the solvents are mixed,
so as to optimise the quality, distribution, size and/or other physical properties of the nano-structured agglomerates produced.

Preferably, forming nano-structured agglomerates comprises optimising and controlling one or more parameters selected from the following group, comprising:
nano-particle and/or agglomerate size;
nano-particle and/or agglomerate distribution;
void fraction of the nano-structured agglomerates; and/or
doping.

Preferably, adding a plurality of dopant atoms, optionally comprising Cs and/or La atoms, prior to agglomeration.

Preferably, the doped nano-structured agglomerates increase and/or decrease the charge carriers within the nano-structured agglomerates.

Preferably, the first and second semiconductor materials are:
organic-organic transport materials;
inorganic-inorganic transport materials; or
organic-inorganic transport materials.

Preferably, the nano-particles comprise:
high-Z nano-particles;
organic nano-particles; or
combinations thereof.

Preferably, the nano-structured agglomerates speed-up and slow-down received radiation, creating one or more, or a plurality of positively or negatively charged puddles within surface structures of the agglomerates.

Preferably, the surface structures of the agglomerates, whether external and/or internal surface structures, interact with incoming radiation to attenuate the radiation and provide improved conversion to positive and negative electrical charges.

Preferably, the nano-structured agglomerates act as local inhomogeneities to attract and concentrate the electric field.

Preferably, nano-structured agglomerates convert said radiation into positive and negative electrical charges in radiation-agglomerate interaction events.

Preferably, forming a matrix by dissolving and dispersing first and second semiconductors in one or more solvents, in which the first and/or second

semiconductors comprise a plurality of nano-particles, as an alternative to separately adding nano-particles.

Preferably, particles of the first and/or second semiconductor material(s) are sized and intended to agglomerate, the first and/or second semiconductor material(s) providing nano-particles for agglomeration without requiring (further) addition of nano-particles to form the matrix.

Preferably, the process further comprising applying the matrix to a substrate, which method comprises one or more of doctor blading, slot die coating, ink jet printing, gravure printing, spray coating, spin coating, drop casting and/or 3D printing.

More generally, interfacial layers, surface modifiers and modulators, bulk modulators and passivators may be used to mop-up some of the recombination pathways and enhance device performance.

The radiation detector may include a current measuring device.

The radiation detector may include a voltage source (such as a battery). The voltage source may be provided to apply an electric field across the radiation detector to assist with sweeping the electrons and holes to the respective electrodes. As noted elsewhere in this description, such a voltage source maybe omitted in some implementations.

The radiation detector may further comprise a wireless transmitter that enables real-time data transmission to a remote computer (for example to enable a record to be maintained of the radiation dose a user of a dosimeter is exposed to over time and/or the generation of a warning mechanism that will inform the user of a potential radiation hazard).

The radiation detector may comprise a display for indicating radiation levels.

Incoming radiation may be converted into positive and negative electrical charges in (single) radiation-agglomerate interaction events.

Current may be generated in response to application of a voltage (from a battery) across the device or, in the absence of an external voltage, owing to built-in potential of the device.

The method may further comprise converting the recorded current into an estimate of a level of radiation.

The matrix may be applied to the substrate using one of a number of techniques, such as doctor blading, slot die coating, ink jet printing, gravure printing, spray coating, spin coating, drop casting and 3D printing. The matrix could be applied by any printing technique, including 3D printing. Printing techniques are not essential, for example pressing the matrix into pellets or tiles is possible, as is evaporation or sputtering.

Advantageously, higher attenuation of an X-ray signal can be attained by reducing the absolute content of the NP material. This may be achieved in two ways.

Firstly, introducing agglomerates of NPs which have, within themselves, pockets or air-gaps, but still take up the dimensional space / volume required or used by apparently larger sized NP distributions. This may be achieved as a result of dielectric inhomogeneity, where the dielectric constant of the material, or relative epsilon, rapidly increases or decreases depending on the constituency of the material. Reference is made to Figure 3a, which is discussed in more detail below. Such a rapid increase or decrease in epsilon results from the absence or presence of materials that interact with the incident electromagnetic waves. The agglomerates

of NPs – which have been termed 'nano-structured agglomerates' in the claims – provide surface fluctuations that interact more strongly with electronic materials and, thereby, provide larger structures having greater surfaces, much like the case of plasmonic structures which have the freedom for surface waves to travel across an external volume of the agglomerated particles which, according to the present invention, now include air or vacuum gaps or voids. Different wavelengths of radiation interact differently with the dimensions of the created agglomerated surfaces, which can be tuned or tailored during creation to detect and resonate with different energy ranges – which is elaborated upon further in the exemplary embodiments.

Secondly, a route to creating extended and enhanced interaction volumes with radiation may be engineered by doping the NPs with additional electron containing or hole containing elements. By 'doping', or increasing / decreasing the charge carriers within the elemental agglomerate loaded to the nano-composite materials, one can increase / decrease interaction volume and plasmonic effects of the enhanced / reduced volumetric regions purely by controlling the dielectric inhomogeneity of the structures. Reference is made to Figure 3b, which is discussed in more detail below. A sudden change in the epsilon of the material, which is linked to charge *via* Gauss' Law, may be given as $\nabla.D=Q$, where ∇ is the function div or divergence as used in Maxwell's law, Q is the total charge and D is the electric flux. D is equal to εE, where ε is the dielectric constant or epsilon of the material (and is a physical parameter that controls the charge transfer fields within electronic thin films), and E is the electric field across the film. This is elaborated upon further in the exemplary embodiments.

In considering mixed phase materials that have doped regions or regions of nano-particles, advantageously, these high-density regions, agglomerates or portions are high-density 'blobs' of material and may act as local inhomogeneities to attract and/or concentrate the electric field which, in so doing, the electric charge collected acts as Mie scatter points that enhance the charge *via* plasmonic effects. Similarly, an absence of material or air-gaps acts as voids of dielectric areas in which the epsilon drops sharply from the surrounding materials, preferably composed of metals with high-epsilon or high-atomic density. This produces a sudden variation in the $\nabla.D$ function that creates either negative or positive charge puddles within the agglomerated-surfaces, that can act as dielectric inhomogeneity points to create disruptive volumes that may interact extensively with radiation and act to attenuate the signal, providing more charge carriers for capture of the signal.

Advantageously, the agglomerates, through lack of continuous particulate matter as demonstrated in meta-surfaces, have appropriately-sized radiation disrupting nano-particle-like surfaces, provide conversion into positive and negative electrical charges. Further advantageously, the agglomerates act as appropriately-sized nano-particles to provide conversion into free positive and negative electrical charges, through direct conversion of radiation.

Advantageously, detection is as a result of ionisation of charge owing to the speeding up, slowing down, or both speeding up and slowing down of radiation when confined within inhomogeneous regions within the agglomerate, where the inhomogeneity is nano-structured within the agglomerate in the form of solid nano-particles, or a void or absence of solid nano-particles / materials within an "active capture cross-section" of a detecting component structured into an electronically active device within a radiation detector system.

Advantageously, when using mixed organic-inorganic transport systems, with materials such as lead-based perovskites as the inorganic component, efficiencies as high as 25% power conversion efficiency have been recorded.

Advantageously, in at least one embodiment, the invention provides a plastic electronic X-ray radiation detector which remains flexible and provides efficient radiation detection, whilst its properties may be optimised or tuned during manufacture at least through NP size, to attenuate an incoming X-ray signal.

Accordingly, those skilled in the art will understand that, for an electromagnetic (EM) wave, the change in the dielectric permittivity, or 'epsilon', will create a delta function of the wave continuity, that will form the basis for perturbation of the EM wave to change its propagation and create attenuation of the signal. The presence of another material, or absence of one, the presence of one or more voids, and/or plurality of such aspects throughout the agglomerate provided in regions and/or interfaces of a size comparable to, or within, a wavelength of the EM wave, causes perturbation of the wave (in those regions) to first slow down or speed up the group velocity of the wave, causing an effect, or effects, detectable as a current.

The invention will now be disclosed, by way of example only, with reference to the following drawings, in which:

Figure 1 is a schematic view of a device according to an embodiment of the present invention;

Figure 2 is a schematic view of a radiation detector including the device of Figure 1;

Figure 3a is a schematic view of an agglomerate of the device of Figure 1;

Figure 3b is a schematic view of a doped agglomerate of the device of Figure 1;

Figure 4 is a flowchart directed to an intended use of the radiation detector of Figure 2;

Figure 5 is a graph showing the effect of Bi_2O_3 NP content on sensitivity;

Figure 6 is a graph showing the effect of Bi_2O_3 nano-particle diameter on sensitivity;

Figure 7 is a graph showing the effect of high-Z material thickness on sensitivity; and

Figure 8 is a graph showing the effect of BHJ thickness for doped Bi_2O_3 on sensitivity.

Figure 1 shows a device, identified generally by reference 1, which includes a bulk material 2 and a plurality of nano-structured agglomerates 3 dispersed in the bulk material 2. The bulk material 2 provides a network having a first semiconductor material for transporting positive electrical charges and a second semiconductor material for transporting negative electrical charges, such that the first and second materials are dispersed within the network to form a plurality of electrical junctions. The nano-structured agglomerates 3, which are shown in more detail in Figures 3a and 3b, are a plurality of agglomerated primary particles 4, having inter-particle pores 5 (voids or gaps) therebetween, the effect of which is to provide in the gaps 5 a different dielectric constant to that of the primary particle 4. Accordingly, the nano-structured agglomerates 3 have a plurality of regions of different relative permittivity capable of creating dielectric inhomogeneities within the nano-structured agglomerates 3. The plurality of regions and/or interfaces of different relative

permittivity may be configured, and predetermined, to have a size comparable to, or within, a wavelength of incoming radiation one wishes to detect. Figure 3a shows non-doped, nano-structured agglomerates 3, whereas Figure 3b shows doped nano-structured agglomerates 3', which additionally includes dopant atoms 6. The dopant 6 is shown in close proximity to a primary nano-particle 4' transferring a negative charge 7 to that primary nano-particle 4' – this being an example of electron transfer through doping. Other effects are, of course, providable through doping, as explained above. The first and second semiconductor materials may be organic-organic transport materials; inorganic-inorganic transport materials; or organic-inorganic transport materials. Interfaces 8 are provided between primary particles 4, dopant atoms 6 and/or inter-particle pores 5. The interfaces are provided: at a juncture of adjoining primary particles 4 (for example as shown in Figures 3a and 3b); at a juncture of primary particles 4 and inter-particle pores 5; at a juncture of primary particles 4 and dopant atoms 6; and/or at a juncture of dopant atoms 6 and inter-particle pores 5.

Through creating agglomerates 3; 3' of NPs 4 which, within themselves, have pockets of air-gaps (voids) 5 and solid NP regions, but still take up the dimensional space or volume of apparently larger sized NP distributions, one creates a volume which, having an absence or presence of material that interacts with the incident electromagnetic wave, has surface fluctuations that interact more strongly with electronic materials and, thereby, create larger apparent surfaces (much like the case of plasmonic structures) providing freedom for surface waves to travel across a larger 'external-volume' of agglomerated particles which includes air or vacuum gaps. As an alternative, one can achieve a similar result through, at least, using different NP sizes, different distributions of NPs, different doping, or different void distributions in the agglomerates to create puddles of charge – the dielectric inhomogeneity creating rapidly changing delta electric flux, changing the charge dynamic statistics.

Figure 2 shows a radiation detector, identified generally by reference 10, which includes device 1, described above with reference to Figure 1. The detector 10 includes a first electrode 11, a second electrode 12, a substrate 13, a current measuring device 14 and a voltage source 15 (such as a battery). As shown in Figure 2, device 1 is sandwiched between the first and second electrodes 11; 12.

As denoted by the arrow 16 in Figure 2, radiation is received at the detector 10. Radiation interacts with device 1 and generates a current that can be detected by the current measuring device 14. The bulk material 2 forms a bulk heterojunction (BHJ) 2. The BHJ 2 is, in this example, an interpenetrating network of an organic hole transporter/p-type semiconductor/electron donor and an organic electron transporter/n-type semiconductor/electron acceptor. Interaction between these electron donor and acceptor materials results in the formation of electrical junctions (or nano-scale diodes) that are present throughout the volume of the device

Close proximity of the electrical junctions to the agglomerates 3 provides a maximum number of charge carriers 17a; 17b to be removed as electrical current (and hence to be detected by the current measuring device 14). In other words, the agglomerates are located in an intrinsically in-built depletion region. The BHJ 2 assists in the removal of charge carriers from the entirety of the active polymer layer. Hence, these systems can be operated under very low voltages (< 10 V), or even at 0 V. Such low voltage operations are ideal, especially in the case of portable radiation monitors that generally require a low voltage source (e.g. the voltage source 15) such as batteries that enable the operation of the detector 10. Greater

thickness of the active layer (~1-100 μm range) may be used to capture a maximum percentage of incident radiation, whilst still providing efficient extraction of the charges towards the electrodes.

Accordingly, it will be understood that nano-particle and/or agglomerate size; nano-particle and/or agglomerate distribution; void fraction of the nano-structured agglomerates; and/or doping are factors that may tailored to provide nano-structured agglomerates having optimised performance characteristics for a specific detection purpose. Such tailoring can produce a multitude of different agglomerate variations of, or having, different dielectric inhomogeneity. Such tailoring may also provide regions and/or interfaces of different relative permittivity, whose size characteristics or dimensions in any given direction are comparable to, or within, a wavelength of the radiation one intends to detect. Further, this provides a great deal of flexibility, including the possibility of tailoring nano-scale structures on surfaces either by design of bottom-up nano-structures or top-down design using block-copolymers of lithography, that may be created over large area substrates using 3-D additive or subtractive lithography.

It should be noted that the use of a voltage source is not essential in all embodiments. Further, the use of a current detector is not essential in all embodiments, since the determination of charge generation can be carried out in other ways.

As the radiation attenuation coefficient of organic materials (i.e. low-Z constituents such as carbon and hydrogen) is low, the BHJ active organic material 2 alone attenuates very little of the incoming radiation. However, the presence of the agglomerates 3; 3' aids attenuating incoming radiation, allowing generation of electrical charge carriers to produce a detectable electrical current. In general terms, the term 'nano-particles' used herein conforms at least to the definition given in the ASTM E2456-06 standard (ASTM E2456-06(2012), Standard Terminology Relating to Nanotechnology, ASTM International, West Conshohocken, PA, 2012, www.astm.org.), such that the term 'nano-particle' generally means a particle having at least one dimension of less than 100nm.

Performance of the detector is typically dependent upon the formation of higher density regions or agglomerates 3; 3'. If the particle size of the first and/or second organic semiconductor is in the quantum regime, i.e. the particle size range where quantum mechanical effects dominate over bulk properties, radiation interaction with the organic semiconductor *per se* provides little if any charge generation, since, generally speaking, organic semiconductors attenuate low levels of radiation.

The agglomerates 3; 3' may also arise as a result of the mixing of solutions used in the production of the donor or acceptor layers or both from solution or evaporation in the case of, say, halide perovskite solar cell production. In this case, a single stage or two-stage process may be used for the production of the layered materials. In the single stage process, a material such as PbI_2 (lead iodide) is mixed with a solvent and, when in liquid-state, mixed further with molecular cations, such as FA (formamidinium lead bromide), MA (methylammonium lead bromide) or a combination of the two. The mixture is applied to a surface that allows the solvent to evaporate and, thereby, form microcrystalline perovskites that can act as a single layer of agglomerates of such a formation of NP, or agglomerates that can be mixed with other organic layered materials. The energy for the inorganic crystal NP nucleation may come from either the solvent evaporation or moderate heating from the substrate to create the dielectrically inhomogeneous mixed material phase

(agglomerates). In the two-stage process, the above process is followed by a secondary interaction with a solution that further precipitates crystallites, using what is commonly referred to as an 'antisolvent' step, a surface modifier, or an interface modulator, that helps create more controlled nucleation of the inorganic crystallites at this layered stage. The two-stage process solvents and modifiers may be added in a single stage, for the single stage nucleation; however this provides less control and uniformity of the layer agglomerates / NPs created from that process. Control of solvents, anti-solvents, cations, anions, temperature, and/or time at which the different components are introduced, the speed at which the solvents are mixed, the environment in which the solvents are mixed, etc. all help control the final quality, distribution, size and physical properties of the materials that are produced and used to attenuate the X-ray radiation in the X-ray devices that are fabricated.

Furthermore, if particle size of agglomerates is too large, this causes inefficient packing within the active material and, consequently, reduces the number of junction diodes within the BHJ 2 local to the agglomerates – thereby reducing the efficiency of the detector. Larger agglomerates may also cause the diode-like behaviour of the device to be affected and cause it to behave as a resistor. So, size of the agglomerates 3; 3' has to be optimum for charge generation and extraction to occur most efficiently.

As the dimensions of the agglomerates are larger compared to the wavelength of the ionizing radiation, the latter undergoes Mie scattering resulting in an increase in the path length. This scattering effect is increase as agglomerate size increases. However, as charge extraction generally takes place at a depth of 10-15 nm, a majority of the deposited energy, i.e. X-ray energy, is converted to heat for larger agglomerates. Further, while charge extraction is more efficient as the agglomerate size decreases, the scattering effect is significantly reduced. Therefore, an agglomerate size in the range of 20-100 nm may be preferred (e.g. for X-ray radiation). The use of agglomerates, as defined herein, also enables broadband sensing of X-rays (i.e. detection of X-rays from 1keV and above) owing to the ionizing radiation scattering effects, being an improvement over current direct X-ray detectors, which are limited to a very narrow energy range (e.g. amorphous selenium which is one of the most widely used direct X-ray detector materials is incapable of detecting X-rays with energies above 50 keV).

The radiation detector 10, preferably directly, converts incident high-energy radiation into a detectable electrical signal, preferably, in one step. In other words, this detection does not involve additional conversion steps such as the generation of visible light, as with scintillator detectors, or the generation of excitons, as seen in scintillator detectors and quantum nano-particle detectors, etc.

As a first example, a single detector can be interfaced with:

- A wireless transmitter that enables real-time data transmission to a remote computer that in turn enables: (i) a record to be maintained of the radiation dose a user of the dosimeter is exposed to over time; and/or (ii) generating a warning mechanism that will inform the user of a potential radiation hazard.
- A system integrated with the detector that either generates a warning signal (noise) and/or consists of a display that indicates the radiation levels in the surroundings.
- A system that combines both the features above.

Examples for powering such systems include an indoor solar cell that harvests light from the lighting conditions in the environment, a battery (e.g. coin cells, flexible or rigid batteries), or an energy storage device such as a

supercapacitor. It is envisaged that this can also be extended to a situation where the power is supplied by a wired connection.

Dosimeter set-up may be extended to integrate multiple detectors each of which can detect either different types of radiation (e.g. neutrons or X-rays), or identify the different energies of a particular radiation or a mixture of both.

The entire system can be integrated either on a rigid backing or a flexible backing such as on a sheet of plastic or a plaster, amongst others.

Furthermore, given that the material of the detector 10 can be made flexible, a dosimeter can be fixed in a location of interest, such as by being wrapped around a pipe.

An optimised detector signal depends upon charge collection. Given the attenuation of radiation throughout the detector, charges need to be collected from the entirety of the active device layer. A single carrier type organic semiconductor system only produces an electrical junction that favours charge extraction at one electrode. Consequently, carriers are only removed at this interface as the opposite electrode acts as a barrier for extraction of the opposite charge – this is only the case if the two contacts have different work functions. The BHJ 2 system as described above produces electrical junctions throughout the active material where charges are extracted through both electrodes. This increases the probability of extraction of both types of charge carriers generated by the high energy radiation. The effects of these mechanisms described above can be seen in the attenuation of typical materials at different photon energies (<0.1 MeV – photo electric effect, 0.1-10 MeV – Compton scattering, and >10 MeV – pair production). These effects are further enhanced by the Mie scattering of ionising radiation that takes place owing to the agglomerates 3; 3' / higher density regions/portions being slightly larger than the wavelength of the ionising radiation / and, of course, the tailored and intended plurality of regions of different relative permittivity, creating dielectric inhomogeneities within the nano-structured agglomerates.

Figure 4 is a flow chart showing an algorithm, indicated generally by reference 40, providing an exemplary use of the radiation detector 10 of Figure 2. Accordingly, radiation detector 10 may work as follows.

Algorithm 40 starts at step 41, where the device 1 is used to attenuate incoming radiation. In this example, agglomerates 3; 3' in the bulk material 2 / BHJ 2 (of device 1) attenuate the incident high-energy radiation. As indicated in step 42, radiation interaction with the agglomerates 3; 3' results in the creation of electron 17b and hole 17a free charge carriers. At step 43, the generated electron 17b and hole 17a free charges are swept through the BHJ 2 towards the electrodes 11 and 12 with the aid of an applied voltage bias (e.g. applied by the voltage source 15, if provided). As an aside, the charges may also be swept out by the in-built potential of the detector enabling the operation under 0 V bias, i.e. omitting the voltage source 15. Charges 17a; 17b, as described above with reference to step 42, are collected at the electrodes 11; 12 and the current is recorded – step 44. Calibration or other processing may be undertaken to relate current output to incident radiation dose. Finally, at step 45, an estimate of the incident radiation is determined, based on the current detected in step 44.

There are many potential applications for detectors, such as radiation detector 10, and one such example is a portable dosimeter.

Experimental Example

The following experimental example utilises a direct radiation detector made from an organic donor and an organic acceptor-based BHJ system. In this exemplary system, poly(3-hexylthiophene-2,5-diyl): [6,6]-Phenyl C71 butyric acid methyl ester (P3HT:PCBM) provides the bulk-heterojunction active material (bulk material 2), and Bismuth Oxide (Bi_2O_3) the high-Z NPs (the nano-particles 4). Aluminium (Al) and indium tin oxide (ITO) are used as the cathode and anode electrodes, respectively (the electrodes 11 and 12 of the detector 10).

By way of a variant, Bi_2O_3 used above may be substituted with other types of high-Z NPs 4, or substituted with other types of agglomerates 3; 3', including both organic or inorganic components, perovskite nano-crystals, perovskite agglomerates, etc.

Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, 40 mg, Rieke 4002 EE) and [6,6]-Phenyl C_{71} butyric acid methyl ester ($PC_{70}BM$, 40 mg, 99% pure; Solenne) were added to 1 ml of dichlorobenzene to produce a P3HT:$PC_{70}BM$ (Bi_2O_3-0) solution. Bi_2O_3 nano-particles 4 (β phase with a tetragonal crystal structure; 38 nm diameter; surface area 18 $m^2\ g^{-1}$; Alfa Aesar) were dispersed in P3HT:$PC_{70}BM$ solution to give a Bi_2O_3 concentration of 40 (Bi_2O_3-40) mg ml^{-1}. The NP weight percentage (wt %) of this is 33%. Agglomeration may initially take place upon dispersing the NP, as the NPs are not perfectly dispersed.

On an ITO (In_2O_3:Sn) glass substrate (15 mm × 15 mm), an electron blocking and hole transporting layer (HTL) of Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS; Al 4083; Heraeus) – or, in variants a Spiro-OMeTAD or P3HT or PTAA layer (see Table of materials shown) – was spin coated in air (at 5000 rpm for 40 s) and annealed at elevated temperature for 10 minutes to give a thickness of 40 nm. A volume of 90 µl of Bi_2O_3-0 and Bi_2O_3-40 solutions were coated and annealed at 60 °C for 20 – 40 minutes under a closed petri dish. Additionally, or alternatively to the above, prior to annealing, agglomerates are formed in the Bi_2O_3-0 and Bi_2O_3-40 layer, as the NPs are not uniformly dispersed. This was followed by annealing at 140 °C for 10 minutes, in a dry nitrogen glovebox. The devices were not placed under a covered petri dish for the second annealing step. Devices were kept under vacuum at a pressure of less than 3×10^{-6} mbar to remove any residual solvent. This was followed by the deposition of an electron transporting (ETL) and hole blocking layer, 1-2.9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP; sublimed grade, Sigma Aldrich, 99.99% purity, 5 nm thickness) and with the deposition of an Al cathode (~120 nm) by evaporation. In variants, the BCP may be substituted with TiO_2, ZnO, C60, PCBM or another ETL layer of equivalent functionality. Device encapsulation was carried out using an encapsulation glass slide and UV light cure adhesive glue (Ossila) illuminated under a UV lamp for 5 minutes. The HTL and ETL, and electrode materials, can be interchanged with any such materials suitable for the application which optimize extraction of charge carriers from the BHJ active material. By way of explanation, prior to annealing, and in the formation stage, the mixture is often termed a matrix. A network, on the other hand, is a term often used to describe the mixture following annealing or after the input of energy to the matrix, when more order is imbued.

The following results were obtained following further analysis and testing.

As shown in Figure 5, the data demonstrates that, for each different particle size and its distribution, there is a peak sensitivity that can be tailored based on the type(s) of material, its size and the energy it is detecting. This lays the foundation for different NP size ranges being understood to be more sensitive to different energy

ranges, especially to those it is designed to detect, and one can further optimise the distribution and aggregation of the NPs according to the desired detection goal of the detector. Further, based upon this principle, holographic and tomographic imaging for hyperspectral ranges may be obtained in a single detector configuration. These agglomerates may also comprise different families of particle sizes, where the composition of the particle size and the 'agglomerate-surface-volume' density will give different attenuation to the radiation that impacts upon the device, structure, or detector.

As shown in Figure 6, which shows a variation in detected sensitivity, sensitivity is affected by size of NP, which is a feature that can be controlled and tailored to the X-ray energy one is wishing to detect – four of which energies are exemplified in Figure 6. Based upon NP diameter and distribution, one can obtain a different sweet-spot or specific sensitivity in the detector, owing to localised dielectric inhomogeneity created within composite detector materials.

Figure 7, shows sensitivity versus volume for high-Z nanomaterials present in a detector material. One skilled in the art will understand that Figure 7 shows there is no simple linear relationship between the X-ray signal attenuation – as found in standard X-ray bulk detectors. The data shows a volume of the high-Z NP in each detector that will attenuate and convert X-ray radiation into current is not a simple volumetric coefficient relationship to the high-Z material content. Accordingly, it will be understood that, although attenuation is an important factor, it is not the only relevant factor, and charge transport and the manner in which charge is created are also important factors.

With respect to Figure 8, this shows the impact of doping of Bi_2O_3 nano-particles with Cs in order to change the charge particles available for conduction by being excited by the irradiating X-rays. This figure also shows that the doping of the carriers, which impacts the dielectric inhomogeneity by varying the dielectric constant, ε, within the material is equally (or in some cases more impactful by also providing free carriers) important to the sensitivity as an X-ray detector. Figure 8 shows, on the one hand, the impact of dopant La (Lanthanum) on X-ray detection within a device structure and, on the other hand, the impact of dopant Cs (Caesium) on X-ray detection within the same device structure. It will be understood that adding La to the Bi_2O_3 NPs creates oxygen vacancies and negatively charged superoxide radicals. This is facilitated by the intermediate La doping band within the Bi_2O_3 that facilitates increased, positively charged holes. It will also be understood that adding Cs to the Bi_2O_3 NPs would not, potentially, provide as many free carriers and may result in a more Coulombic interaction of Cs to the oxygen vacancies – thereby, preventing less free charge. This is observed in the higher detected sensitivity with La doped Bi_2O_3 NPs as compared to Cs doped Bi_2O_3 NPs.

The above seeks to exemplify the importance of choosing the correct dopant, together with the correct concentration and optimum dielectric to create the best inhomogeneity for X-ray detector fabrication. Naturally, such factors can be differently optimised to detect different radiation.

Owing to mechanical flexibility of the device or radiation detector, it can be folded. Hence, multiple layers of a polymer/organic semiconductor/agglomerate film can be used to attenuate even more of the incident radiation. Improvement of the charge generation and collection from these light-weight, flexible organic semiconductor/polymer/agglomerate materials would potentially allow for their

integration into disposable adherent plasters to allow for short duration, real-time detection/imaging of radiation beams.

Organic semiconducting diodes lend themselves to a high spatial resolution and can adapt to directional dependence. Organic semiconductor or polymer diodes can be produced with sub-micrometre dimensions, over large areas, and on flexible substrates, and a combination of these technologies allows them to be positioned three-dimensionally in an incident radiation beam. As dose is a one-dimensional quantity, a dosimeter with a small volume has a high spatial resolution. The ability to 'fold' a single polymer organic semiconductor detector so that the incident beam passes through it multiple times allows for greater detector sensitivity. Finally, the rugged, solid-state, semiconducting organic diodes offer the advantage of a real-time electrical response, which can be directly read out, and low operating voltages, which may allow them to be battery operated, increasing their portability.

It should be noted that other materials that can be used as the cathode include n-type graphene, n-type carbon nanotubes, chromium, titanium, calcium, barium or similar materials with low-work function as well as bilayer cathode systems that include a metal/metal oxide combinations where the metal oxide can be zinc oxide, titanium oxide, chromium oxide or metal/organic combinations where the organic system can be bathocuproine of polyethyleneimine or its derivatives, poly fluorines such as (PFN).

Other materials that can be used as the anode include high-work function materials such as gold, nickel, graphene, combinations of metal/metal oxides where the metal oxide can be based on tungsten, molybdenum, nickel or metal/organic where the organic can be PEDOT:PSS, PTAA, F8T2, spiro-MEOTAD, P3HT, or any p-type polymer, where the SAM can be 2PACz, 4PACz or any high work function type SAM.

For fabrication, active material deposition for large area production can be carried out using different roll-to-roll or sheet-to-sheet coating techniques such as, spray coating, slot-die coating, ink-jet printing, gravure printing, flexographic printing, power pressing, etc. It should be noted that the invention is applicable to detection of other ionising (e.g. nuclear) radiation such as alpha particles, beta particles, neutrons and gamma rays while retaining the same configuration. This can be achieved by using an appropriate agglomerate. For neutron detection, layers of Gadolinium or doped diamond and nanocrystalline diamond films can be used. For gamma ray detection, high-Z NPs above Z=13 like bismuth, tantalum, tungsten, lead, gold, platinum can be used and alloys such as cadmium telluride (CdTe), perovskites (lead based and others) and compound high-Z NPs such as Bi_2O_3 etc. nanodiamonds etc. For alpha and beta particle detection, any carbon-based material can be used including graphene, amorphous carbon, carbon nanotubes and all allotropes of carbon. Si-based NPs and nanowires, Silver (Ag) based NPs and nanowires, Zinc (Zn) NPs and any type of metals and alloys (NPs or micron size particles) may be used for alpha and beta particle detection.

As described above, radiation detectors described herein include a network having a first material for transporting positive electric charges and a second material for transporting negative electric charge, with agglomerates being dispersed within the network.

The radiation detector may be referred to in some embodiments as a radiation imager. The radiation imager may include appropriate read-out electronics. Such a radiation imager has many potential applications, as set out below.

- The imager may be fabricated either on a flexible backing (substrate, plaster for example) and used, for example, for wearable health monitoring applications. For example, a patch can be envisaged which is worn by a user over an area where there is wound or area where bone damage has been detected or over an area where cancerous tissues are present. Owing to the highly sensitive nature of each detector pixel, a small X-ray source can be used to periodically observe the healing of wounds, broken bones or any changes in the cancerous tissue.
- The imager may also be used for monitoring metallic objects in environments in which they should not be present. For example, these imagers can be used in food packaging industry to identify potential metallic contaminants in food. Furthermore, through use of multi-channel analysing techniques or other appropriate techniques, the imager can also be used to map out which element is present and where.
- The technology is applicable to security screening activities at airports, ports, and suspected bomb-sites, as examples.
- The technology can be used for non-destructive evaluation of mechanical components either during manufacture, or during specified evaluation periods for components in operation or for real-time monitoring of the health of the mechanical components by integration into the system itself. The potential flexible nature of the imager enables the advantages of X-ray films (very little restrictions in terms of shapes that can be imaged) to be used, but in a digital form (real-time imaging possibly as opposed to film where real-time imaging is not possible).
- The detector and imager would be suitable for academic research.

The above applications are not restricted to the use of X-rays but also applicable to cases where other form(s) of ionising radiation is/are used.

In fabricating the detectors, the solution consisting of the mixture of first and second materials (such as hole transporting organic semiconductor (or multiple hole transporting semiconductors) and electron transporting semiconductor (or multiple electron transporting semiconductors)) and agglomerates can be:

- Deposited directly from solution using solution printing and coating techniques, such as but not limited to slot die coating, doctor blading, gravure printing, flexographic printing, drop casting, 3-D printing, inkjet printing, spray coating, or dip coating on a flexible or rigid substrate – furthermore, these inks can also be used to coat wires or filaments as well;
- Deposited directly onto a substrate through thermal evaporation, chemical vapour deposition, pulsed laser ablation, or sputter coating techniques;
- Formed into free standing pellets or tiles through the following processing: an anti-solvent in which the organic semiconductors are soluble, but which is at least partially miscible with the organic solvent used is introduced to the ink resulting in the materials used crashing out of the system – the remaining solvent can then be evaporated to obtain a dry powder which can be pressed and sintered if necessary to form a solid, free standing pellet;
- The ink containing the semiconductor can be sprayed under high pressure to a low vacuum system maintained at an appropriate pressure where the

solvent is evaporated and the powder is collected – the powder can then be pressed to form a free standing pellet; or

- The pellet could be pressed onto a substrate consisting of the appropriate electrical contact material or a backplane as described under the X-ray imager.

The physical properties of an ink can also be tuned to enable filaments of this X-ray detector being formed such as through extrusion or electrospinning.

There are provided below, tables of exemplary materials for use as the first and second organic semiconductor materials (i.e. hole and electron transporting materials) and the nano-particles.

Exemplary hole transporting material:

Abbreviated name	**Full name**
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PCDTBT	Poly[*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)], Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]
PCPDTBT	Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]
Si-PCPDTBT	poly[2,6-(4,4-bis-(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)]
PTB7	Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PCE10, PBDTTT-EFT, PBDTT-FTTE, PTB7-Th	Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)]
PCE11, PFFBT4T-2OD	Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3'''-di(2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)]
DPP-DTT, PDBT-co-DTT, PTT-DTDPP, PDPP-DTT, DPPTT-TT, DPP-TTT, PDPP2T-TT, PDPP2T-TT-OD	Poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)]
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
PPDT2FBT	poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)]
PCE12, PBDB-T	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
DTS(FBTTh$_2$)$_2$, F-DTS, p-DTS(FBTTh$_2$)$_2$	7,7′-[4,4-Bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2,6-diyl]bis[6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole]

PCDTFBT (PFT-100)	Poly[(5-fluoro-2,1,3-benzothiadiazole-4,7-diyl)(4,4-dihexadecyl-4H- cyclopenta[2,1-b:3,4- b']dithiophene-2,6-diyl)(6-fluoro-2,1,3-benzothiadiazole- 4,7-diyl)(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)]
Materials with an ABX_3 structure as an active layer or nano-particle additive	Where ABX_3 can be considered as a metal-halide perovskite material, with A= cation such as Cs^+, FA^+ (formamidinium ($CH(NH2)2^+$, abbreviated FA^+), MA^+ (methylammonium ($CH3NH3^+$)) or a combination of the same ; B= metal cation such as Pb^+, Sn^+, Ge^+ or a combination of the same; and X= is an anion halogen such as I^-, Cl^-, Br^- or a combination of the same.
Materials with an $A_2B^IB^{III}X_6$ structure as an active layer or nano-particle additive	Where $A_2B^IB^{III}X_6$ can be considered as a double metal-halide perovskite material, with A= cation such as Cs^+, Li^+, MA^+ (methylammonium ($CH3NH3^+$)) or a combination of the same; B^I= is a monovalent metal cation such as Ag^+, Au^+, Ti, NH_4^+ Ge^+ or a combination of the same; B^{III}= is a trivalent metal cation such as Cu^{3+}, Bi^{3+}, Fe^{3+}, Yb^{3+}, In^{3+}, Sb^{3+}, or a combination of the same; and X= is an anion halogen such as F^-, I^-, Cl^-, Br^-, CN^- or a combination of the same.
PTAA	Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine
TIPS-Pentacene	6,13-Bis(triisopropylsilylethynyl)pentacene
NiO nano-particle	Nickel oxide
CuSCN	Copper Thiocynate
MoO_3 nano-particle	Molybedenum trioxide
V_2O_5	Vernadium pentoxide

Exemplary electron transporting materials:

Abbreviated name	**Full name**
PC60BM,PC61BM, 60PCBM, PCBM	[6,6]-Phenyl-C61-butyric acid methyl ester
PC70BM,PC71BM, 70PCBM	[6,6]-Phenyl-C61-butyric acid methyl ester
ZnO nano-particle	Zinc oxide
TiO2	Titanium oxide
FBR	(5*Z*,5′*Z*)-5,5′-{(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis[2,1,3-benzothiadiazole-7,4-diyl(*Z*)methylylidene]}bis(3-ethyl-2-thioxo-1,3-thiazolidin-4-one)
O-IDTBR	(5Z,5'Z)-5,5'-((7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)
ITIC	3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene

ICBA, ICBA60	1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno[5,6]fullerene-C60
ICBA70	1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno[5,6]fullerene-C70
P(NDI2OD-T2), N2200, Polynaphtalene-bithiophene	Poly{[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}
PNDI-2F, P(NDI2OD-T2F), PNDI(2OD)2T-2F	Poly[[1,2,3,6,7,8-hexahydro-2,7-bis(2-octyldodecyl)-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-4,9-diyl](3,3'-difluoro[2,2'-bithiophene]-5,5'-diyl)]
DPPDPyBT	Poly(2,5-bis(2-octyldodecyl)-3,6-di(pyridin-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-2,2'-bithiophene)

Exemplary radiation attenuating materials (i.e. as nano-structured agglomerates):

Abbreviated name	**Full name**
Bi_2O_3	bismuth oxide
BiI3	bismuth iodide
BiOCl	bismuth oxichloride
TiO_2	titanium oxide
Ta_2O_5	tantalum oxide
WO_3	tungsten oxide
CdTe	cadmium telluride
HgTe	mercury telluride
	diamond
PbS	lead sulfide
PbSe	lead selenide
ABX_3 where A can be methylammonium, formamidinium, caesium, rubidium etc., B is lead, X can be iodine or bromine	Lead halide perovskites
$A_2B^IB^{III}X_6$ where A can be methylammonium, formamidinium, caesium; B^I is silver Ag; B^{III} is Bi; X can be iodine or bromine	Silver – Bismuth double metal-halide perovskite

The following statements summarise some interesting aspects of at least some of the embodiments described herein.

Performance of the detector is typically dependent upon the agglomerate size, distribution and positioning in the detector. Owing to the larger size of the agglomerate as compared to the wavelength of the ionizing radiation, the latter undergoes scattering (e.g. Mie scattering) resulting in an increase in the path length. An agglomerate particle size in the range of 20-100 nm may be preferred (e.g. for X-ray radiation). The use of agglomerates as defined herein also enables broadband sensing of X-rays (i.e. detection of X-rays from 1keV and above) owing to the ionizing radiation scattering effects. Cf., those skilled in the art will know that the sensitivities of current direct X-ray detectors are limited to a very narrow energy range (e.g. amorphous selenium which is one of the most widely used direct X-ray detector materials is incapable of detecting X-rays with energies above 50 keV).

However, according to the invention – in which the agglomerate is provided with suitable dielectric inhomogeneity – it is understood the detector may be used to detect X-ray energies below 50 keV, and detector efficiency and sensitivity in any energy range may be improved, based upon the principles of the present invention.

Radiation detectors described herein may use an ink consisting of at least two organic semiconductors, one which when processed into a solid state semiconductor preferentially transports positive charges (holes) and another which preferentially transports negative charges (electrons) to separate electrical contacts. In the field of organic photovoltaics as well as photodetectors (detecting UV to the near infrared portion of the electromagnetic spectrum), a mixture of organic semiconductors such as those indicated above is used. Inorganic NPs and agglomerates too may be used in such a detector, based upon the dielectric inhomogeneity it will possess. This mixture is often referred to as a bulk heterojunction (BHJ). The interaction of photons in the energy range of UV to the near infrared portion of the electromagnetic spectrum results in the formation of bound electrons and holes which are known as excitons. In organic photovoltaics and photodetectors, this BHJ architecture is required for breaking (or dissociation) of the exciton into free charge prior to being swept away through the electron and hole transporting organic semiconductors (often referred to as acceptor phase and donor phase, specifically in exciton based systems only). Although the mixture of organic semiconductors and agglomerates described herein may not partake in exciton dissociation in a direct radiation detector , the mixture can still be referred to as providing a bulk heterojunction in view of the formation of a built-in electric field. Alternatively, the same bulk heterojunction may also be referred to as a p-n junction, an interpenetrating p-n junction, an interpenetrating network of percolated electron and hole transporting phases or a donor (referring to the hole transporting organic semiconductor) – acceptor (referring to the electron transporting organic semiconductor) system.

The number of organic semiconductors used may be increased provided that they do not impede the charge transport highlighted above. Furthermore, the organic semiconductors identified herein can be polymers, small molecules, o-dimensional, 1-dimensional, 2-dimensional or 3-dimensional structures.

The semiconductors indicated herein may also be selected such that the combination of organic semiconductors, inorganic semiconductors, or the combination of organic and inorganic semiconductors and agglomerates results in the formation of a built-in electric field which drives the free electrons and holes generated upon the interaction of incident X-rays with the agglomerates to separate electrical contacts resulting in an electrical signal (even in the absence of an external voltage bias). In other words, use of the above combination of semiconductors enables a fully depleted diode even in the absence of an external electrical field. The mixture of electron and hole transporting materials (such as organic semiconductors) used enables the extraction of X-ray generated free carriers (even in the absence of an external bias).

The nano-particles used maybe of a single material type or maybe a mixture of nano-particles consisting of different high-Z materials. A single nano-particle may also consist of two high-Z materials provided that the materials are selected such that both the electron and hole extraction is not impeded. The layering of one high-Z material on another high-Z material may be carried out in a manner such that, even within the nano-particle itself, a field acts to efficiently extract the charges directly generated upon interaction with ionizing radiation.

Preparation of the solid state detector may be carried out through the direct coating of the ink using techniques such as doctor blading, slot die coating, ink jet printing, gravure printing, spray coating, spin coating, drop casting, etc. Furthermore, the solid state detector can be fabricated by the preparation of organic, inorganic or a mixture of organic and inorganic semiconductor powders, which are obtained by adding an anti-solvent to the ink resulting in the sedimentation of the organic semiconductor-agglomerate mix, followed by the removal of the solvents using roto-evaporation, drying in air or vacuum drying to obtain a powder. This powder can be pressed to any required size to form a solid state disk / pellet / slab / tile / wafer which, in combination with appropriate electrical contacts for the selective extraction of electrons and holes at separate surfaces or at separate regions in the same surface or a combination of both, enables the entirety to act as an ionizing radiation detector.

Interesting aspects of at least some embodiments described herein include:

- The formation of nano-structured agglomerates to provide conversion into positive and negative electrical charges.
- The formation of nano-structured agglomerates to provide conversion into free positive and negative electrical charges, through direct conversion of radiation.
- Improved attenuation of radiation energy through the formation of dielectric inhomogeneities in the formed nano-structured agglomerates.
- The broadband response of the detector owing to the scattering effects prevalent for all X-ray energies above 1 keV.
- The use of at least two organic semiconductors where one semiconductor preferentially transports holes whilst the other transports electrons.
- The use of at least two inorganic semiconductors, or an inorganic and organic pair, where one semiconductor preferentially transports holes whilst the other transports electrons.
- The use of the semiconductor system indicated herein which results in a built-in-field within the device enabling the operation of the detector even in the absence of an external voltage bias.

Claims:

1.) A device for converting incoming radiation into positive and negative electrical charges, the device comprising:
a network comprising:
a first semiconductor material for transporting positive electrical charges; and
a second semiconductor material for transporting negative electrical charges,
the first and second semiconductor materials being dispersed within the network to provide a plurality of electrical junctions,
wherein, the network further comprises a plurality of nano-structured agglomerates dispersed within the network, the nano-structured agglomerates comprise a plurality of regions and/or interfaces of different relative permittivity capable of creating dielectric inhomogeneities within the nano-structured agglomerates.

2.) A device as claimed in claim 1, wherein, the nano-structured agglomerates comprise:
a) a plurality of regions and/or interfaces of different relative permittivity comparable to, or within, a wavelength of said incoming radiation; and/or
b) a porosity or void fraction of about 0.01 to about 0.99, of about 0.05 to about 0.7, or about 0.1 to about 0.3.

3.) A device as claimed in claim 1 or claim 2, wherein, the nano-structured agglomerates comprise:
one or more, or a plurality of, solid nano-particle structures; and
one or more, or a plurality of, voids between the one or more, or plurality of, solid nano-particle structures.

4.) A device as claimed in any preceding claims, wherein the nano-structured agglomerates are configured to speed-up and slow-down received radiation, creating one or more, or a plurality of positively or negatively charged puddles within surface structures of the agglomerates.

5.) A device as claimed in any preceding claim, wherein the surface structures of the nano-structured agglomerates, whether external and/or internal surface structures, are configured to interact with incoming radiation to attenuate the radiation and provide improved conversion to positive and negative electrical charges.

6.) A device as claimed in any preceding claim, wherein the plurality of nano-structured agglomerates are configured to:
act as local inhomogeneities capable of attracting and concentrating the electric field; and/or
convert said radiation into positive and negative electrical charges in radiation-agglomerate interaction events.

7.) A device as claimed in any preceding claim, wherein the plurality of nano-structured agglomerates are doped nano-structured agglomerates, having additional electron-containing or hole-containing elements.

8.) A device as claimed in claim 7, wherein the plurality of nano-structured agglomerates are doped with Caesium (Cs) and/or Lanthanum (La).

9.) A device as claimed in any preceding claim, wherein the plurality of nano-structured agglomerates comprises optimised parameters of one or more of the following group, comprising:
nano-particle and/or agglomerate size;
nano-particle and/or agglomerate distribution;
void fraction of the nano-structured agglomerates; and/or
doping.

10.) A device as claimed in any preceding claim, wherein the first and second semiconductor materials comprise:
organic-organic transport materials;
inorganic-inorganic transport materials; or
organic-inorganic transport materials.

11.) A device as claimed in any preceding claim, wherein the nano-particles comprise:
high-Z nano-particles;
organic nano-particles; or
combinations thereof.

12.) A device as claimed in any preceding claim, wherein parameters of the nano-structured agglomerates are configured to be actively optimised for detection of defined wavelengths or forms of radiation intended to be detected by the device.

13.) A device as claimed in any preceding claim, wherein, the first semiconductor material comprises P3HT, the second semiconductor material comprises PCBM, and the nano-particles comprise Bi_2O_3, optionally doped with Caesium (Cs) and/or Lanthanum (La).

14.) A radiation detector comprising:
a first electrode;
a second electrode; and
a device as claimed in any one of claims 1 to 13 located or sandwiched between the first and second electrodes.

15.) A system comprising a plurality of radiation detectors as claimed in claim 14, wherein at least some of the plurality of radiation detectors are configured to:
detect multiple different types of radiation;
detect one type of radiation; and/or
identify or detect different energies of a particular radiation.

16.) A method comprising: using a device as claimed in any one of claims 1 to 13, a radiation detector as claimed in claim 14, or a system as claimed in claim 15 to convert incoming radiation into positive and negative electrical charges; and recording a characteristic generated by the positive and negative electrical charges.

17.) A method as claimed in claim 16, further comprising converting the incoming radiation into free positive and negative electrical charges in radiation-agglomerate interaction events.

18.) A method as claimed in claim 16 or claim 17 comprising generating current in response to application of a voltage across the device and converting recorded current into an estimate of a level of incoming radiation.

19.) A process for providing a network for a device for converting incoming radiation into positive and negative electrical charges, the process comprising:
dissolving first and second semiconductors in one or more solvents, the first and second semiconductors being capable of transporting positive and negative electrical charges, respectively;
adding a plurality of nano-particles and dispersing the plurality of nano-particles to form a matrix; and
agglomerating the nano-particles in the matrix to form a plurality of nano-structured agglomerates, the nano-structured agglomerates comprising a plurality of regions and/or interfaces of different relative permittivity, being capable of creating dielectric inhomogeneities within the nano-structured agglomerates.

20.) A process as claimed in claim 19 comprising creating:
a plurality of regions and/or interfaces of different relative permittivity comparable to, or within, a wavelength of said incoming radiation;
one or more, or a plurality of, solid nano-particle structures; and
one or more, or a plurality of, voids between the one or more, or plurality of solid nano-particles structures.

21.) A process as claimed in claim 19 or claim 20, wherein the nano-structured agglomerates are formed:
at least partially within the matrix, prior to application to a substrate; and/or
during layering of the matrix upon a/the substrate.

22.) A process as claimed in any one of claims 19 to 21, wherein agglomeration comprises optimising and controlling:
nano-particle and/or agglomerate size;
nano-particle and/or agglomerate distribution;
void fraction of the nano-structured agglomerates;
doping;
solvents, anti-solvents, cations, anions, temperature and/or time at which different components are introduced;
a speed at which the solvents are mixed; and/or
an environment in which the solvents are mixed,
so as to optimise the quality, distribution, size and/or other physical properties of the nano-structured agglomerates produced.

23.) A process as claimed in any one of claims 19 to 22 comprising adding a plurality of dopant atoms, optionally comprising Cs or La atoms, prior to agglomeration.

24.) A process as claimed in any one of claims 19 to 23 comprising forming a matrix by dissolving and dispersing first and second semiconductors in one or more solvents, in which the first and/or second semiconductors comprise a plurality of nano-particles.

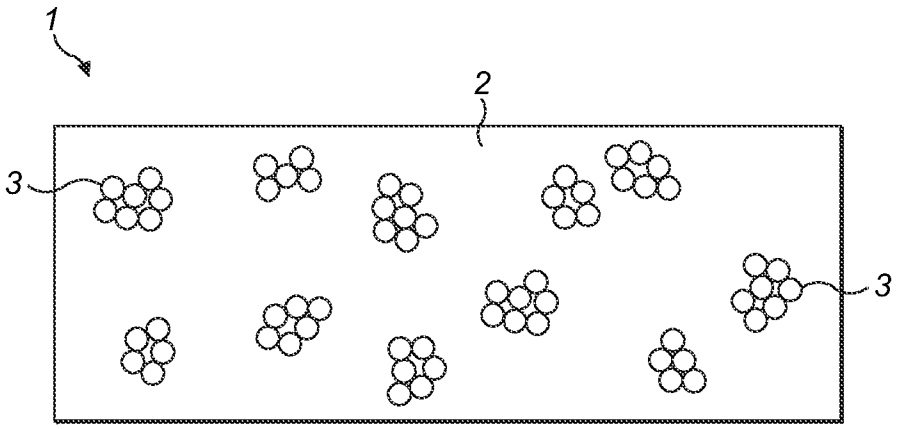

FIG. 1

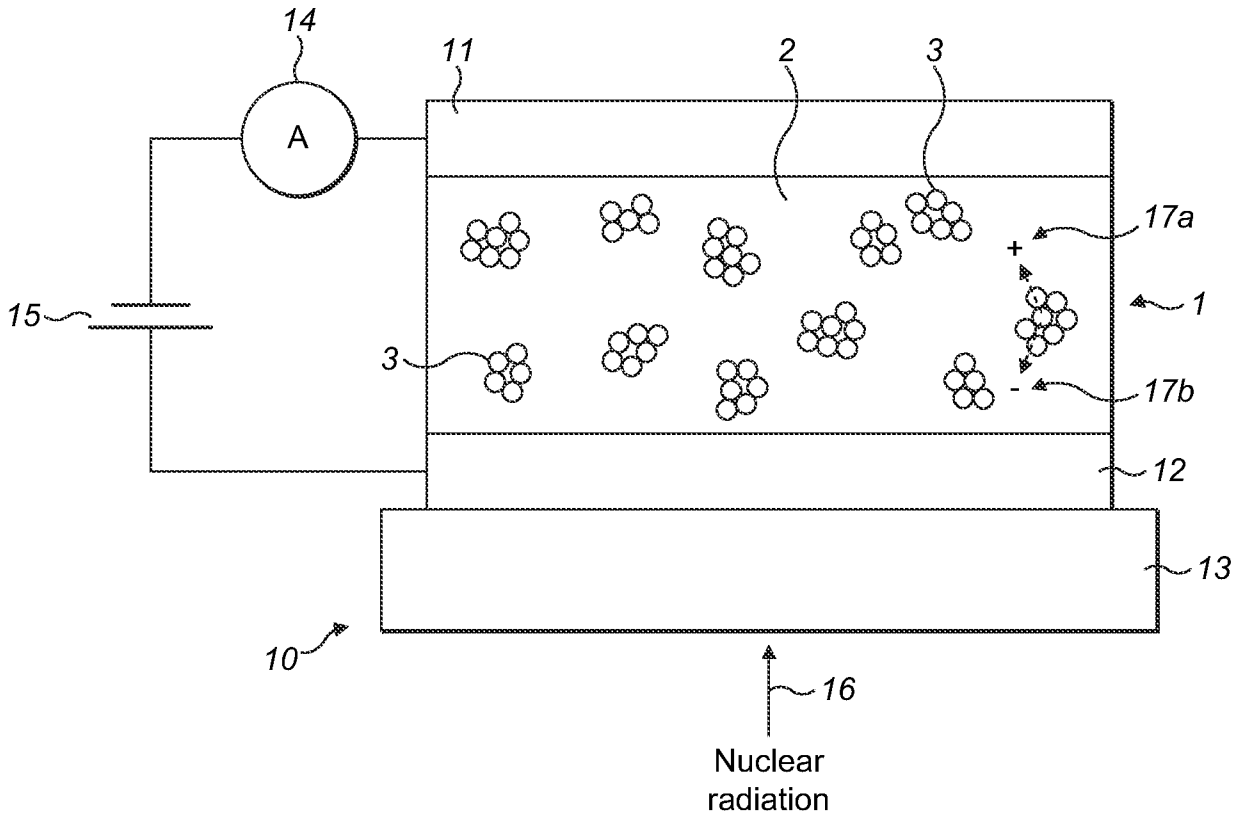

FIG. 2

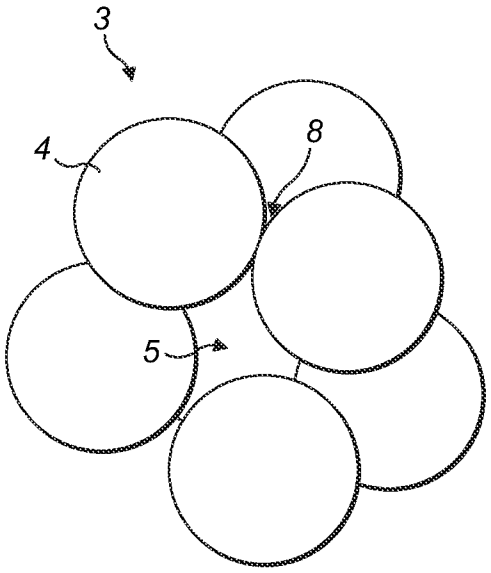

FIG. 3a

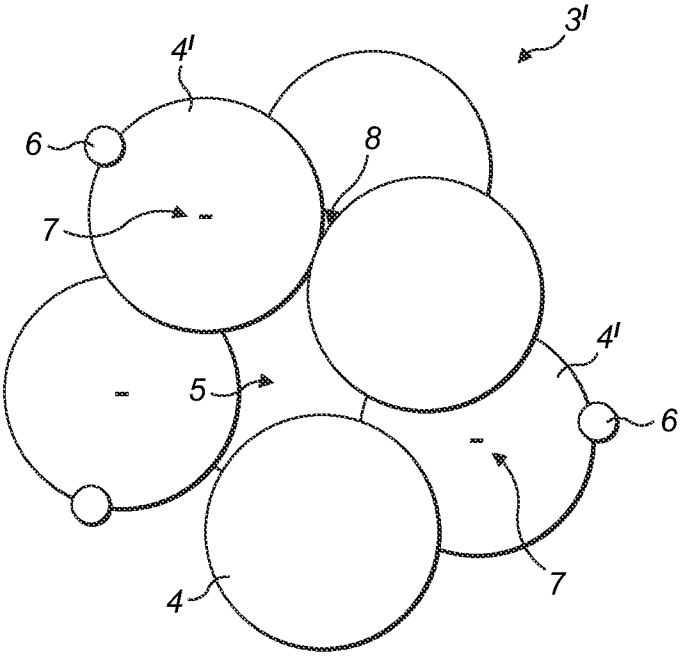

FIG. 3b

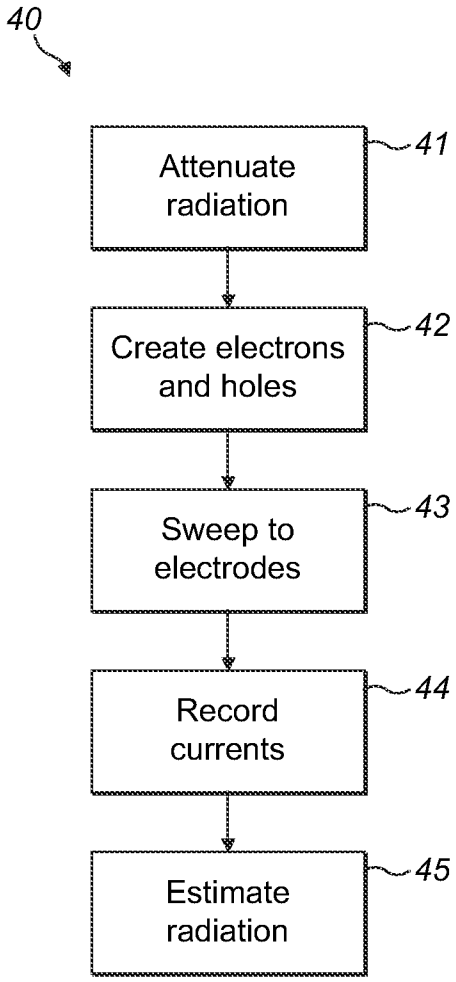
40
Attenuate radiation
41
Create electrons and holes
42
Sweep to electrodes
43
Record currents
44
Estimate radiation
45

FIG. 4

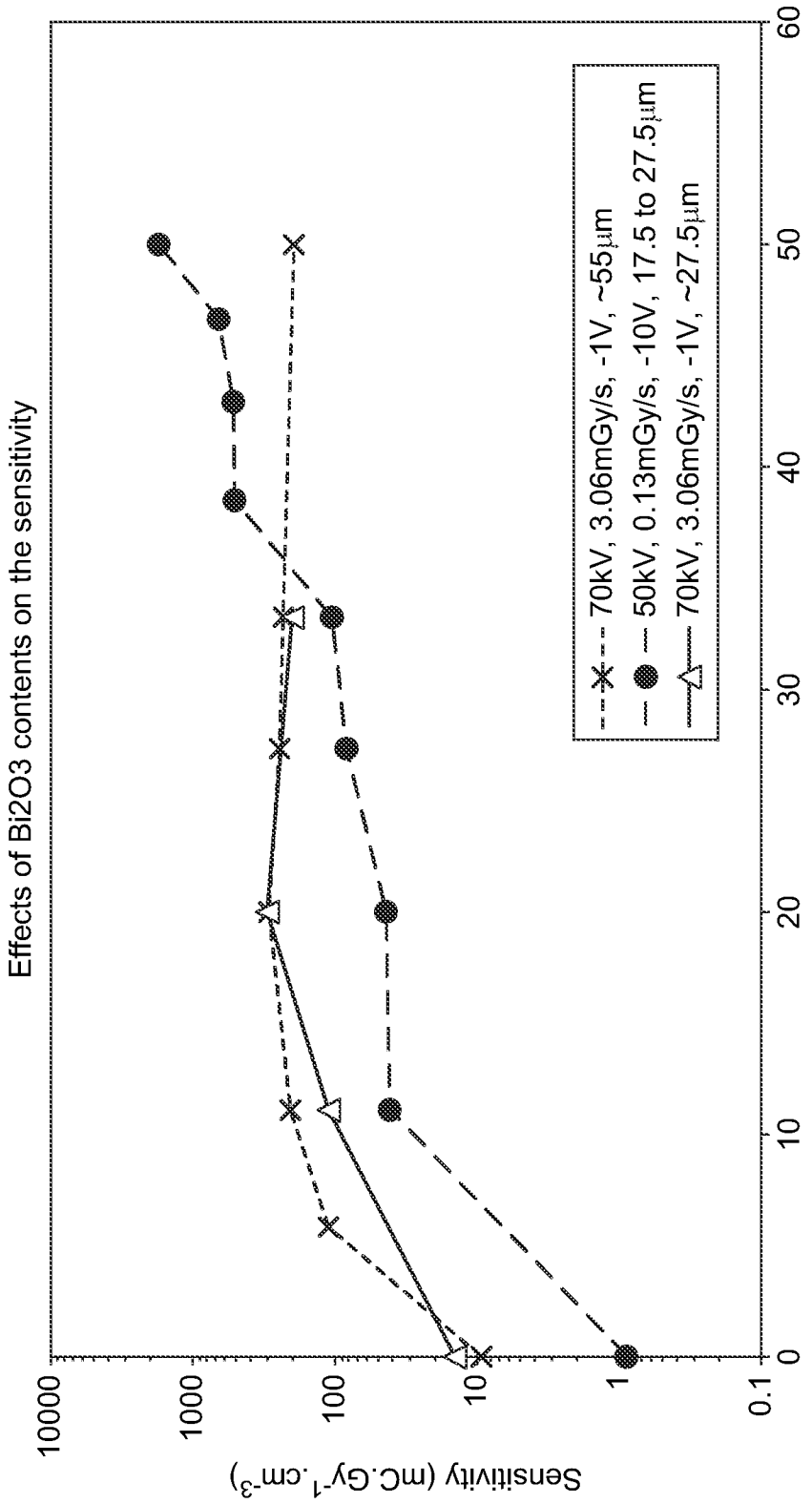
Effects of Bi2O3 contents on the sensitivity
Sensitivity (mC.Gy-1.cm-3)
10000
1000
100
10
1
0.1
0
10
20
30
40
50
60
Bi2O3 nanoparticle (wt%)
70kV, 3.06mGy/s, -1V, ~55μm
50kV, 0.13mGy/s, -10V, 17.5 to 27.5μm
70kV, 3.06mGy/s, -1V, ~27.5μm

FIG. 5

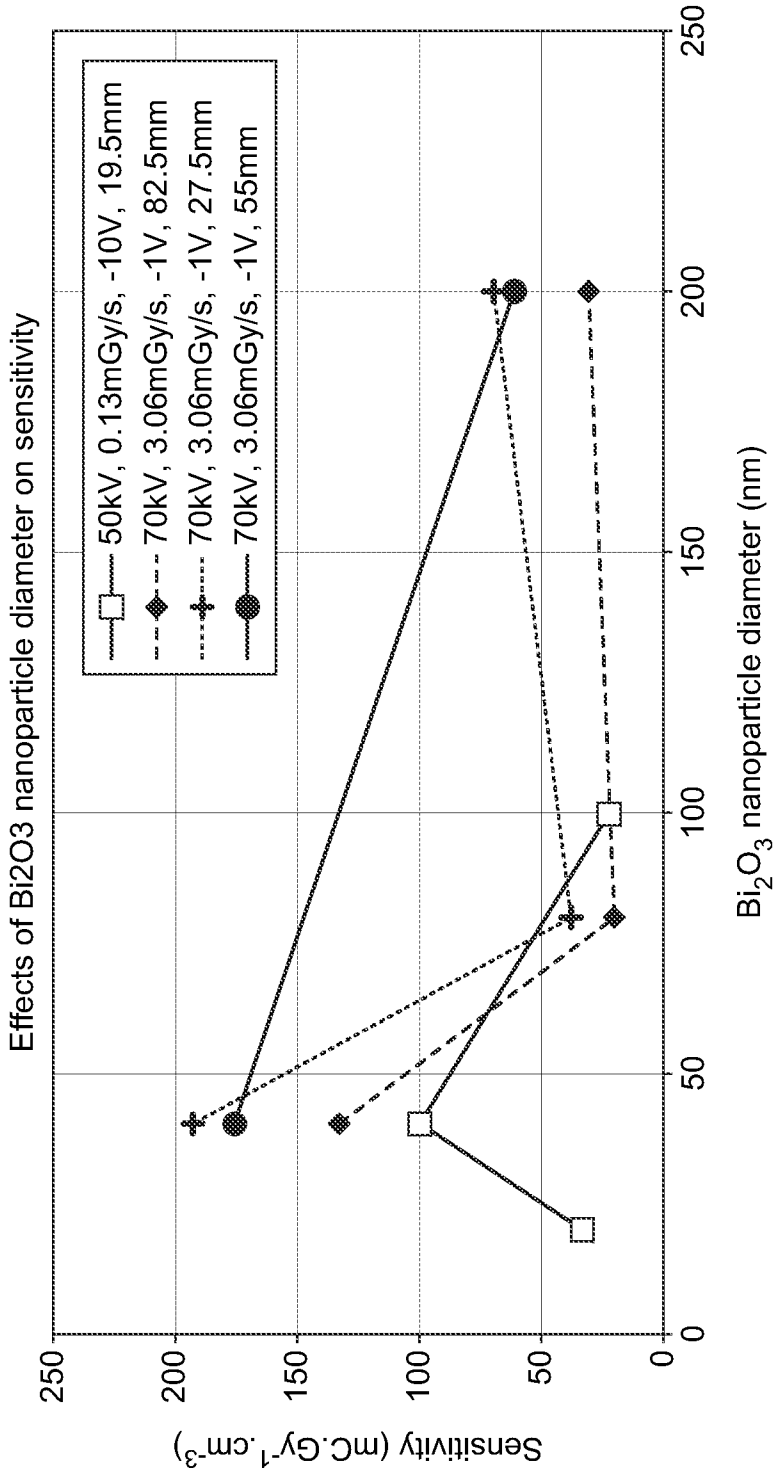
Effects of Bi2O3 nanoparticle diameter on sensitivity
50kV, 0.13mGy/s, -10V, 19.5mm
70kV, 3.06mGy/s, -1V, 82.5mm
70kV, 3.06mGy/s, -1V, 27.5mm
70kV, 3.06mGy/s, -1V, 55mm
Sensitivity (mC.Gy-1.cm-3)
Bi2O3 nanoparticle diameter (nm)
0
50
100
150
200
250

FIG. 6

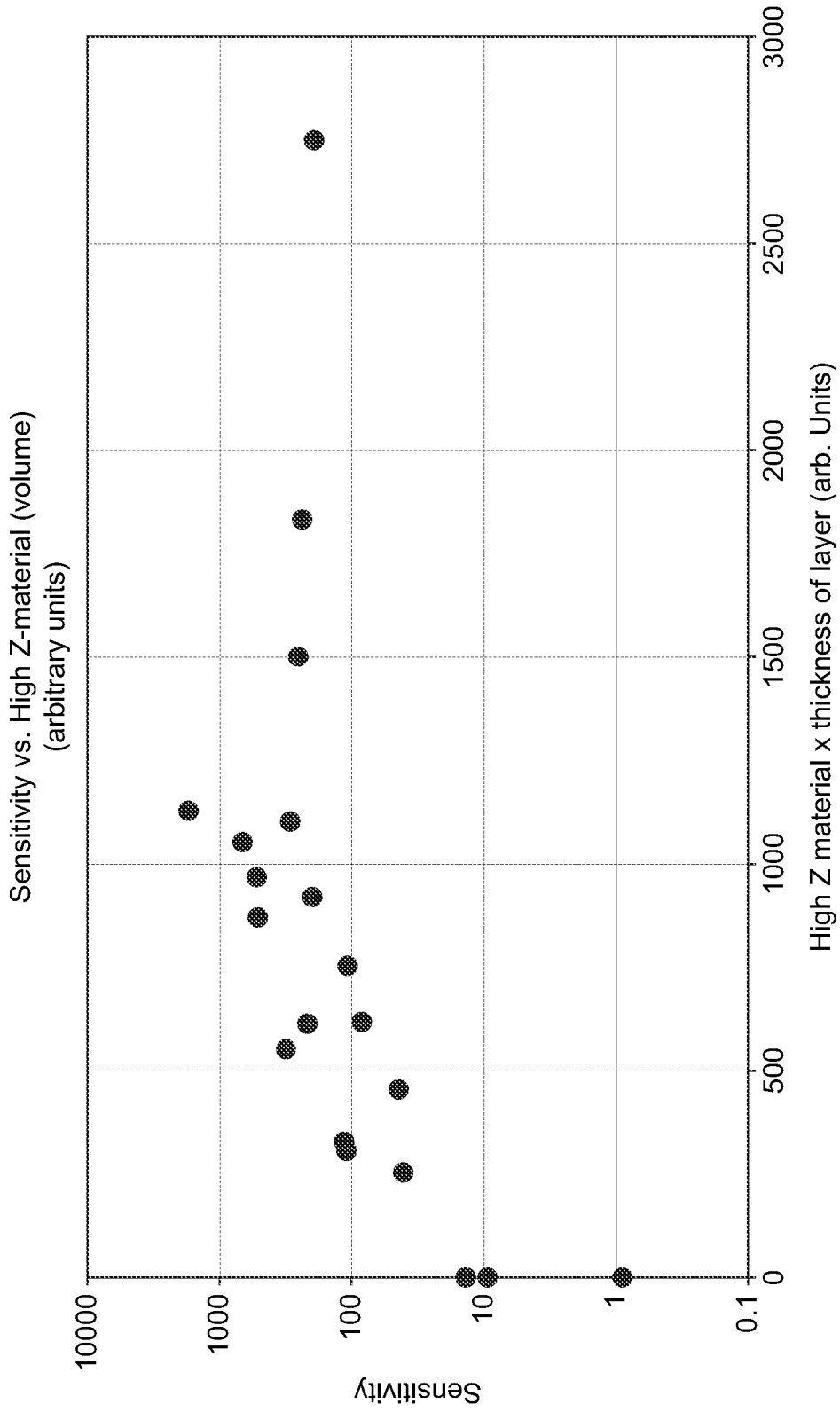
Sensitivity vs. High Z-material (volume)
(arbitrary units)
Sensitivity
10000
1000
100
10
1
0.1
0
500
1000
1500
2000
2500
3000
High Z material x thickness of layer (arb. Units)

FIG. 7

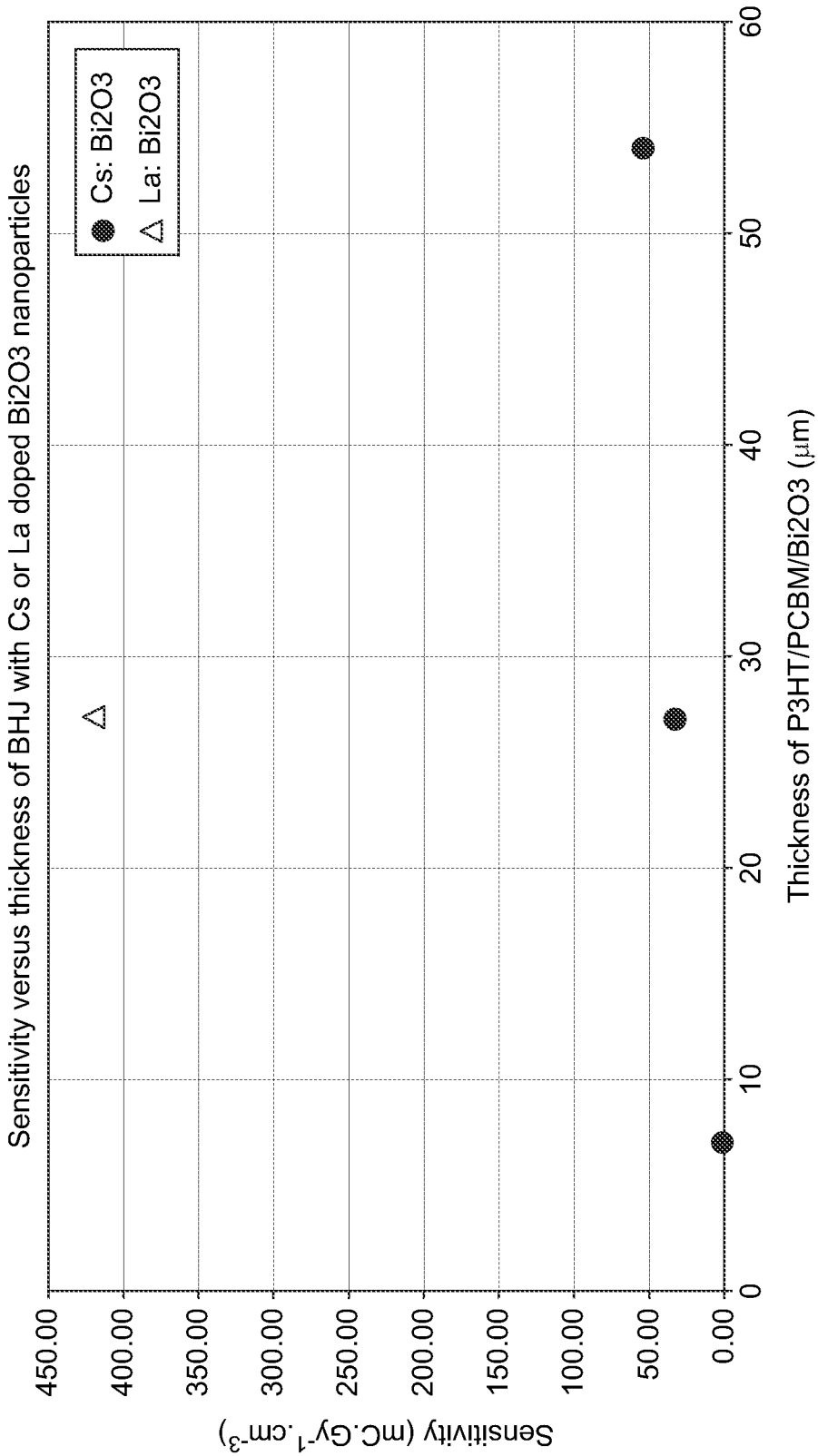
Sensitivity versus thickness of BHJ with Cs or La doped Bi2O3 nanoparticles
Cs: Bi2O3
La: Bi2O3
Sensitivity (mC.Gy-1.cm-3)
450.00
400.00
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
0
10
20
30
40
50
60
Thickness of P3HT/PCBM/Bi2O3 (μm)

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051733

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01T1/24 H10K30/35
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01T H10K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2014 225542 A1 (SIEMENS HEALTHCARE GMBH [DE]) 16 June 2016 (2016-06-16)	1-6,9, 10,12, 16,19, 20,22
A	paragraphs [0028], [0047] - [0048], [0073], [0089], [0090], [0029], [0079], [0010], [0013], [0014], [0065]	7,8,23

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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 September 2024	04/10/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Eberle, Katja

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051733

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MINWOO NAM ET AL: "Efficiency enhancement in organic solar cells by configuring hybrid interfaces with narrow bandgap PbSSe nanocrystals", ORGANIC ELECTRONICS, ELSEVIER, AMSTERDAM, NL, vol. 13, no. 9, 18 April 2012 (2012-04-18) , pages 1546-1552, XP028505135, ISSN: 1566-1199, DOI: 10.1016/J.ORGEL.2012.04.028 [retrieved on 2012-05-17]	1-6, 9-12, 14-22,24
A	abstract; figures page 1549, left-hand column page 1547, right-hand column, paragraphs 2., 3.	7,8,23

X	THIRIMANNE HASHINI M ET AL: "Hybrid Multipixel Array X-Ray Detectors for Real-Time Direct Detection of Hard X-Rays", IEEE TRANSACTIONS ON NUCLEAR SCIENCE, IEEE, USA, vol. 67, no. 10, 2 September 2020 (2020-09-02), pages 2238-2245, XP011814967, ISSN: 0018-9499, DOI: 10.1109/TNS.2020.3021612 [retrieved on 2020-10-16]	1-6, 9-13, 15-20, 22,24
A	abstract; figures page 2239, right-hand column, paragraph II.A	7,8,23

X	VIKRAMAN DHANASEKARAN ET AL: "Influence of morphological tuned nanostructure hybrid layers on efficient bulk heterojunction organic solar cell and X-ray detector performances", APPLIED SURFACE SCIENCE,, vol. 543, 28 December 2020 (2020-12-28), XP086465439, DOI: 10.1016/J.APSUSC.2020.148863 [retrieved on 2020-12-28]	1-6, 9-12, 15-20, 22,24
A	page 2, left-hand column, last paragraph - right-hand column, paragraph f page 2, right-hand column, paragraphs 2.1, 2.2	7,8,23

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2024/051733

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102014225542 A1	16-06-2016	NONE	